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DIFFERENTIATION OF THE COMPONENTS OF AN "EXPLOSIVE OIL": A SURVEY OF THE CHEMICAL LITERATURE

BY

WILLIAM M. THORNTON, JR.

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DIFFERENTIATION OF THE COMPONENTS OF AN "EXPLOSIVE OIL": A SURVEY OF THE CHEMICAL LITERATURE[1]

By William M. Thornton, Jr.[2]

INTRODUCTION

Owing to the comparatively high freezing point of nitroglycerin (14, 15, 16, 17, 18, 23, 37, 38)[3] - 1.9° C. and 13.0° C. for the labile and stabile modifications, respectively, as determined by Hibbert (16) - manufacturers of dynamites have incorporated into the liquid portion of these composite explosives various substances capable of participating in an explosion, to depress the above-mentioned freezing point. Aromatic nitrocompounds, chiefly nitrobenzenes, nitrotoluenes, and nitronaphthalenes, have been used to a considerable extent (51), but such nitrosubstitution products have not proved altogether satisfactory, as has been shown clearly by Naoúm (34). Consequently there has been a strong tendency in recent years to replace them with one or more of several nitric esters, among which the following (29, 35) have been prominent: Dinitrochlorhydrin (monochlorhydrin dinitrate); nitrosugars, for example, sucrose octanitrate (19); tetranitrodiglycerin (diglycerin tetranitrate); nitroglycol (ethyleneglycol dinitrate); and diethyleneglycol dinitrate (13, 46, 47). Of these, nitroglycol (33, 41, 43, 45, 48, 49, 65) is outstanding in importance.

As the Bureau of Mines is naturally interested in the analytical chemistry of the "explosive oils," it seemed desirable to bring together in this report the widely scattered experimental work covering the problem of differentiation that has appeared in various chemical and physicochemical publications.

OUTLINE OF ANALYTICAL PROBLEM

Apart from the determination of moisture, the analysis of dynamites (and permissible explosives) consists in removing the constituents, group by group, with appropriate solvents (56), whereupon the matter taken out in each extraction may be examined further. The first solvent to be applied is generally ether, which dissolves completely the nitric esters and aromatic nitrocompounds and, incidentally, any resins or greases that may be present - also sulfur in moderate amount. After the ether is expelled by evaporation at a low temperature, the weight of the dried residue is recorded. In like manner, a duplicate sample is extracted in order that material may be available for estimation of the sulfur, resins, etc. (54, 58, 61, 64). Disregarding, for the time being, the latter substances, which are apt to be present in small amounts only, there is still the possibility that the "explosive oil" may be composed of one or more of the aromatic nitrocompounds, which may exist in both the solid and the liquid phase; moreover, at least one of the other nitric esters may be dissolved in the nitroglycerin. In fact, one separated "oil" was found to contain five ingredients: Nitroglycerin, nitroglycol, nitrosugar, tetranitrodiglycerin, and nitrotoluenes (according to a communication from J. E. Crawshaw, Bureau of Mines, Explosives Experiment Station, Bruceton, Pa., March 21, 1940); however, this degree of complexity is very unusual. As indicated, the true nitrobodies are used much less nowadays than formerly, and of the esters dinitrochlorhydrin and tetranitrodiglycerin are said to be less efficient as depressants than nitroglycol (31, 48). Even when the preliminary examination has shown that the nitrosubstitution compounds are absent, differentiation of two or more of these aliphatic nitrate esters is no easy task, for it cannot be said, all things being taken into account, that any really satisfactory analytical process that is applicable in the case is yet known.

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[1] The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7145."

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[3] Numbers underscored in parentheses refer to bibliography at end of this report.

DETERMINATION OF THE AROMATIC NITROCOMPOUNDS (AS A GROUP)

1. The nitric nitrogen may be determined by any of several methods (conveniently with the nitrometer), and the weight of the "explosive oil" as a whole being known, that of the nitrocompounds may be calculated (59). It is obvious, however, that until such a procedure can be amplified it is limited to mixtures in which only one ester of established identity (say nitroglycerin) is present. Moreover, the nitrometer should not be employed if mononitrobodies form part of the material under test, seeing that, under the prevailing conditions, further nitration has been demonstrated to take place with some of these substances (50, 52). It is also interesting to note, in passing, that nitroamines (8) evolve nitric oxide when in contact with mercury and sulfuric acid.

2. The total quantity of nitrogen may be determined by Kjeldahl's process, suitably modified (7, 10, 60), and the nitric nitrogen, which has been estimated independently, may be deducted from this total. The remainder is the nitrogen of the nitrosubstitution compounds (59).

3. Another procedure for determining the entire quantity of nitrogen has been developed by Berl and Jurrissen (2), in which they make use of their "Zersetzungskolben," or decomposition flask (cf. 8) - an instrument that serves much the same purpose as the generating bulb of a nitrometer (57). After a preliminary treatment with chromic and sulfuric acids, all of the

nitrogen is converted to nitric oxide regardless of its mode of linkage in the original compounds.

4. An ingenious method for separating nitrosubstitution compounds from nitroglycerin has been reported by Hyde (22). The process depends upon the preferential solvent action of carbon bisulfide on the true nitrocompounds and similarly that of aqueous acetic acid (about 75 percent) on nitroglycerin, the two liquids being nearly immiscible. Hyde's test analyses, in which he employed several different nitrobodies, are excellent, but as he experimented with no nitric esters except nitroglycerin, little or nothing seems to be known regarding the deportment of the other organic nitrates now being used in explosives. Furthermore, the apparatus of Hyde (22) is rather elaborate and the technique exacting. Naturally, these characteristics have not tended to make the method popular.

5. Busch's reagent ("nitron") is available for gravimetric estimation of nitric acid and its inorganic salts; hence any nitric ester that can be saponified satisfactorily may be determined with its aid. "Nitron" is a basic organic compound having the formula $C_{20}H_{16}N_4$, whose nitrate is only very sparingly soluble in water. Although certain nitrocompounds give no precipitate with this reagent and may therefore be expected to pass into the filtrate, others yield insoluble addition compounds, as pointed out by Cope and Barab (9). Accordingly, this chemical has very restricted applicability, as far as the parting of these two classes of organic substances is concerned.

6. A method that permits gravimetric determination of nitrobody mixtures is that of Dickson and Easterbrook (12). In accordance with their adopted procedure, the residue from the ether extract is dissolved in methyl alcohol, which prevents further nitration of the nitrocompounds, and the nitroglycerin is decomposed with ferrous chloride in the presence of hydrochloric acid. The reactions take place at room temperature but require some 24 hours for completion. The resulting solution is extracted with ether, and this extract is washed free of iron salts, dried, and filtered. The ether is removed by evaporation, and the remaining substances (nitrocompounds, presumably) are weighed after being thoroughly desiccated *in vacuo* over sulfuric acid. The results obtained by Dickson and Easterbrook (12) reveal only a fair degree of accuracy.

7. The oxidimetric estimation of the nitric acid that forms when a nitrate ester undergoes hydrolysis has been studied by several investigators. Obviously, when an iron compound is used, the unoxidized ferrous salt may be titrated with a standard oxidizing solution, as originally proposed by Pelouze (40, 63), or the ferric salt resulting from the reaction may be determined with a reducing solution of known titer, after the manner of Braun (4). Aromatic nitrocompounds do not interfere; apparently they remain unaffected.

(a) Pursuant to work by Phelps (42), Huff and Leitch (20) have treated certain nitric esters with an acidified solution of ferrous sulfate in a flask from which the air has been expelled by steam (generated by boiling a portion of water within the receptacle). In the presence of an abundant supply of hydrochloric acid and at a high enough temperature, the desired deoxidation takes place and, as it would appear, goes eventually to completion. After evaporating the reaction mixture to a small volume and partly neutralizing the acid with sodium carbonate, the operator titrates the remaining ferrous salt with a standard solution of potassium permanganate under the well-known optimum conditions.

Results obtained on mannite hexanitrate (alone or in admixture with a nitrocompound) are very satisfactory, whereas those with glycerin trinitrate are somewhat too low. Huff and Leitch have sought to explain these deficiencies on the ground that the vapor tension of nitroglycerin (30) is very appreciable at 100° C. Furthermore, they have suggested certain changes in the foregoing technique that would seem to be sufficiently remedial.

(b) Becker (1), utilizing a standardized solution of titanous chloride (24), has worked out a volumetric method that provides for the determination of both an aliphatic nitrate and an aromatic nitrocompound. A reflux condenser is attached to the reaction flask to prevent the escape of the reducible substances, and a current of carbon dioxide protects the sensitive deoxidizing solutions; even so, it is necessary to make certain small corrections, depending on control experiments.

A synopsis of Becker's procedure (1) follows: Virturally theoretical results for nitroglycerol and for ethyleneglycol dinitrate may be obtained by dissolving the sample in acetic acid, adding an excess of ferrous chloride, introducing hydrochloric acid, boiling, and titrating the resulting ferric iron with a titanous chloride solution of known normality. Ammonium thiocyanate serves as the indicator in the preceding titration. When present in admixture, 2,4-dinitrotoluene does not interfere and may be accurately determined in the residual solution by reduction with titanous chloride in the customary way. When a small quantity is present, diethyldiphenylurea or diphenylamine exerts no disturbing action.

(c) In this connection, it is interesting to notice that Kolthoff, Sandell, and Moskovitz (25) claim that the reduction of nitric acid by ferrous chloride, which is a slow reaction ordinarily, is greatly hastened by the addition of a small amount of ammonium molybdate.

DIFFERENTIATION OF NITRIC ESTERS

Only one of the foregoing processes for distinguishing quantitatively between the nitric esters and the aromatic nitrocompounds, the method of Hyde (22), leaves the ester chemically intact. Even here, any further treatment of the ester, dissolved in aqueous acetic acid, would seem to be difficult. Accordingly, attempts to differentiate between any two organic nitrates in an "explosive oil" appear to involve either of two assumptions: namely, that the nitroderivatives are absent or that, if present, they exert but little interfering action in the proposed procedure. (As Storm (53) has pointed out, several of the nitrobodies are only partly soluble in nitroglycerin.)

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The aliphatic nitrate esters and the aromatic nitrocompounds exhibit distinct differences in chemical behavior, whereas the esters - with the exception of nitrosucrose and the like, and dinitrochlorhydrin - are very similar one to another. Thus far, then, physicochemical methods usually have been brought to bear upon the problem of differentiating the latter substances. Among the physical properties that have been considered as suited to the purpose, are the following: Mean molecular weight, solubility, rate of evaporation, refractive index, vapor tension, and specific rotatory power with respect to polarized light.

1. Two researches are recorded in the literature in which the ratio by weight of nitroglycerin to another nitric ester, when the two are present in admixture, has been calculated from the mean molecular weight or directly from the data required for establishing this mean molecular weight. Both the elevation of the boiling point (21) and the depression of the freezing point (26) have been utilized, a suitable solvent being selected in any particular case.

(a) As early as 1912, Hyde (21) obtained some promising results in studying mixtures of nitroglycerin and tetranitrodiglycerin by measuring the rise in the boiling point of ethyl acetate (77.15° C. at 760 mm. pressure for the pure liquid) when a weighed quantity of the material under examination was added to a known quantity of the solvent. It is worthy of remark that Hyde (21) operated with solutions considerably more concentrated than those ordinarily used in work of this kind. For example, in his best experiment, in which he obtained 229 as the molecular weight of glyceryl trinitrate (instead of the theoretical number 227.1), he added the ester in the proportion of 34.66 grams to 100 grams of the solvent and observed an increase of 3.95° C. in the boiling point of the acetate. For an obvious reason, he determined the boiling point of the solvent and that of the solution in two separate experiments, dissolving the nitric ester in a fresh, cool portion of the ethyl acetate. The molecular weight may be computed by the formula:

$$M = gr/a,$$

where $\underline{g}$ is grams of ester per 100 grams of solvent, $\underline{a}$ is the increase in boiling point, and $\underline{r}$ is a constant whose value depends on the solvent (26.1 for ethyl acetate).

Hyde's results for the molecular weight of nitroglycerin range from 229 (as given above) to 235, and it is more than conceivable that these high numbers are due to some association of the dissolved molecules. In applying the method to the analysis of a mixture supposed to contain nitroglycerin and tetranitrodiglycerin, which had been extracted from an explosive, he concluded that the mixture comprised 29 percent of the more complex ester. An independent value, calculated from the proportion of nitrogen, as obtained with a nitrometer, was 33 percent. The agreement seems reasonably good, especially in view of the fact that a departure of only 0.1 percent from the true nitrogen content causes an error of more than 4 percent in the reported quantity of tetranitrodiglycerin. Closely comparable results have been published by Storm (55).

(b) Marqueyrol and Goutal (26) have studied the effect produced by mixtures of nitroglycerin and nitroglycol on the freezing point of benzene, and they find that the depression of this temperature (5.493° C. for the pure liquid saturated with air) decreases almost linearly with increase in the percentage of nitroglycerin. These investigators also consider the influence of several substances that may be present in the "oil" extracted from certain explosives. Of these, vaseline and dinitrotoluene (1 : 2 : 4) separate in the solid form to a large extent (53), hence the relatively pure liquid portion may be removed with a pipette before the cryoscopic experiment is made. On the contrary, diphenylamine and the substituted ureas remain in solution. In either event, the lowering of the freezing temperature of the solvent does not seem to be seriously vitiated by the "foreign" body, whether the ester is nitroglycerin or nitroglycol; consequently, in accordance with their data, satisfactory approximations may be expected.

It is feasible, of course, to calculate the mean molecular weight in the well-known manner. Thus, if w grams of a substance, when dissolved in W grams of a solvent, lowers the freezing point of the solvent d°, then the molecular weight of the solute is obtained by substituting in the expression:

$$M = kw/dW,$$

where k is a constant depending only on the solvent (5,120 for benzene). Marqueyrol and Goutal (26) evidently prefer to proceed empirically. By dissolving 1 gram of the sample to 10 grams of the solvent in every test, they obtain depressions of the freezing point of benzene that are strictly comparable. Under these conditions, the freezing point is lowered 2.13° C. for nitroglycerin and 3.06° C. for nitroglycol.

Rinkenbach (44) has criticized the cryoscopic method of Marqueyrol and Goutal (26) unfavorably. He makes the following statement: "While fairly accurate for mixtures of the pure substances, it yields very erroneous results when applied to mixtures extracted from commercial explosives." He is inclined to regard unremoved oils, fats, and resins as the disturbing factors.

2. Storm (55) has called attention to the greater solubility of nitroglycerin in dilute acetic acid (60 volumes of glacial acid to 40 volumes of water) as compared with nitropolyglycerin (tetranitrodiglycerin). One gram of nitroglycerin dissolves completely in about 10.5 ml. of the dilute acetic acid, but nitropolyglycerin is much less soluble. By adding the acid to a weighed quantity of the mixed esters, in small increments and with thorough agitation after each addition, the operator may dissolve virtually all the nitroglycerin and leave the nitropolyglycerin in nearly pure condition. Storm (55) treated about 5 grams of an "explosive oil" containing approximately 2 parts by weight of nitroglycerin and 1 part of tetranitrodiglycerin with 150 ml. of the dilute acetic acid. In other words, he employed nearly three

times the amount of acid needed to dissolve 5 grams of pure nitroglycerin. If the residual ester is washed and dried and if a nitrogen determination is made upon it, the value obtained should agree substantially with the theoretical percentage of that element in tetranitrodiglycerin. Speaking more broadly, if tetranitrodiglycerin has been identified by observing its resistance to dissolution in aqueous acetic acid, even though the quantity has not been estimated exactly enough, the analyst can calculate the ratio in which the two esters exist in the mixture from the nitrogen content of the original "oil" - a quantity that, presumably, has been previously established. (See following section.) In the practical application of this process, Storm (55) obtained a result that is satisfactorily compatible with the result he obtained using the technique of Hyde (21).

Determination of Two Components in an "Explosive Oil" by Indirect Analysis: Calculations

Let x = weight of nitroglycerin in mixture and y = weight of tetranitrodiglycerin in mixture.

Similarly, let n_1 = weight of nitrogen in nitroglycerin and n_2 = weight of nitrogen in tetranitrodiglycerin.

Finally, let W = weight of mixture and N = total weight of nitrogen in mixture.

As the percentage of nitrogen in nitroglycerin is 18.51 and in tetranitrodiglycerin is 16.19, n_1 and n_2 may be expressed in terms of x and y, respectively:

$$n_1 = 0.1851x \text{ and } n_2 = 0.1619y.$$

The simultaneous equations are:

$$0.1851x + 0.1619y = N$$
$$x + y = W.$$

Solving for x (N and W being known) gives

$$x = (N - 0.1619W)/0.0232, \text{ and}$$
$$y = W - x.$$

3. In keeping with the great difference in volatility (3, 5, 6, 11, 27, 36, 39, 43) between nitroglycerin and nitroglycol, Marqueyrol and Goutal (26) have found that the ratio in which these two esters are mixed may be determined, at least roughly, by noting the loss in weight under fixed conditions. The material under test is placed in a crystallizing dish 60 mm. in diameter and 35 mm. in height, previously tared, and this receptacle is set in a desiccator containing sulfuric acid. Normal atmospheric pressure and an average temperature of 12° C. are maintained. Under these circumstances, nitroglycerin alone undergoes no sensible loss during 20 days, whereas nitroglycol loses regularly 12 mg. in 24 hours. For mixtures of the two substances the loss is proportional to the content of nitroglycol.

4. Rinkenbach (43, 44, 46) has determined the refractive indices of a number of the aliphatic nitrates at several temperatures, likewise the indices of certain pairs of the nitrates when they form a homogeneous mixture. Among these findings there are a few points that demand attention. The index of refraction for diethyleneglycol dinitrate (1.4536 at 15° C.) is only slightly higher than that of its congener, nitroglycol. On the contrary, a mixture of 70 percent nitroglycerin and 30 percent nitropolyglycerin has a refractive index (1.4767 at 15° C.) even higher than that of nitroglycerin alone. Hence it should be possible to decide, with the aid of a refractometer, whether or not the nitrated glycols are present in a particular sample. Furthermore, Rinkenbach (44) has tabulated his data (see table 1) for mixtures of ethyleneglycol dinitrate (0 to 100 percent) and nitroglycerin (100 to 0 percent). Obviously, as soon as the refractive index of the two nitrates (mixed in unknown ratio) has been obtained experimentally, deduction of the percentage of each component is in order.

TABLE 1. - Refractive indices of mixtures of ethyleneglycol dinitrate and nitroglycerin[1]

Ethyleneglycol dinitrate, percent	Nitroglycerin, percent	n_D^{15}	n_D^{20}	n_D^{25}
0	100	1.4751	1.4732	1.4713
10	90	1.4722	1.4703	1.4684
20	80	1.4694	1.4675	1.4656
30	70	1.4666	1.4648	1.4628
40	60	1.4640	1.4621	1.4601
50	50	1.4613	1.4595	1.4575
60	40	1.4587	1.4569	1.4548
70	30	1.4562	1.4544	1.4523
80	20	1.4537	1.4520	1.4498
90	10	1.4513	1.4496	1.4476
100	0	1.4491	1.4472	1.4454

[1] Rinkenbach, W. H., Analysis of Mixtures of Aliphatic Nitrates by Means of the Refractometer: Ind. Eng. Chem., vol. 19, 1927, p. 1291.

Rinkenbach (44) found, however, that the nitroglycerin extracted from a dynamite showed an abnormally high index of refraction, presumably owing to the presence of oily, fatty, and resinous matter, which freezing and filtering did not remove entirely. He decided, therefore, to recommend the refractometer either for the qualitative detection of the nitrates of the glycols or for factory-control work.

5. The vapor tension of nitroglycerin and of certain allied substances has been determined by a number of investigators (3, 5, 6, 11, 27, 36, 39, 43); unfortunately, however, their published findings, insofar as they are comparable, frequently fail to agree. If the most recent work, that of Brandner (3), be taken as reliable, some interesting conclusions follow. Within the

temperature range of 10° to 50° C. the vapor tension of ethyleneglycol dinitrate is about 100 times that of glycerin trinitrate. These two esters form **approximately** ideal solutions.

As Brandner (3) has measured the tension of various mixtures of nitroglycol and nitroglycerin at several temperatures, it would seem that these data (see table 2) might be utilized for purposes of analysis, provided the experimental difficulties connected with determining the vapor tension of such mixtures are not too great.

TABLE 2. - Vapor pressures of nitroglycerin-nitroglycol solutions1/

Nitroglycol, percent	Total vapor pressure, mm. Hg		
	10° C.	30° C.	50° C.
0...............	0.0001	0.0011	0.0081
10...............	.0027	.0186	.1002
20...............	.0051	.0345	.1841
30...............	.0073	.0490	.2608
40...............	.0093	.0624	.3314

1/ Abridged from table IV of Brandner, J. D., Nitroglycerin and Ethyleneglycol Dinitrate. Vapor Pressures of Binary Solutions: Ind. Eng. Chem., vol. 30, 1938, p. 684.

6. The nitrosugars differ from most organic nitrates that have been used as explosives in that they have some highly characteristic properties. These carbohydrate nitrates, like the naturally occurring sugars, are optically active. Hoffman and Hawse (19), as part of an extensive study of nitrosucrose (sucrose octanitrate), have found its specific rotatory power to be 56.05° at 20° C. With this datum available, the proportion of nitrosucrose, dissolved in nitroglycerin, may be approximated by means of the polarimeter.

7. Apart from its optical activity, nitrosucrose exhibits a definite chemical behavior. According to Taylor and Rinkenbach (62), a portion of the residual "oil" from the ether extract is dissolved in methyl alcohol, and this solution is treated with a little zinc dust and dilute hydrochloric acid. After the action has ceased the solids are allowed to settle, and the supernatant liquid is decanted and tested with Fehling's reagent. A bright-red precipitate of cuprous oxide indicates reducing sugar (derived from the original nitrosugar). In lieu of zinc and acid, ammonium sulfide may be employed as the deoxidizing agent, according to a communication from J. E. Crawshaw, Bureau of Mines, Explosives Experiment Station, Bruceton, Pa., March 21, 1940. The present writer is unaware of any attempt to extend this procedure to the quantitative estimation of a nitrosugar.

It is apparent that evaluation of the chlorine in an "oil" containing dinitrochlorhydrin will enable the analyst to calculate the quantity of the ester (28). But as dinitrochlorhydrin is an uncommon ingredient in blasting explosives manufactured in the United States it is accorded only passing attention here.

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CONCLUSIONS

It is evident that differentiation of the components of an "explosive oil" presents an analytical problem of great difficulty. The author of this report has endeavored to bring to light such groundwork as previous investigators have recorded in the chemical literature. It is hoped that a truly satisfactory structure can now be reared upon this foundation.

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